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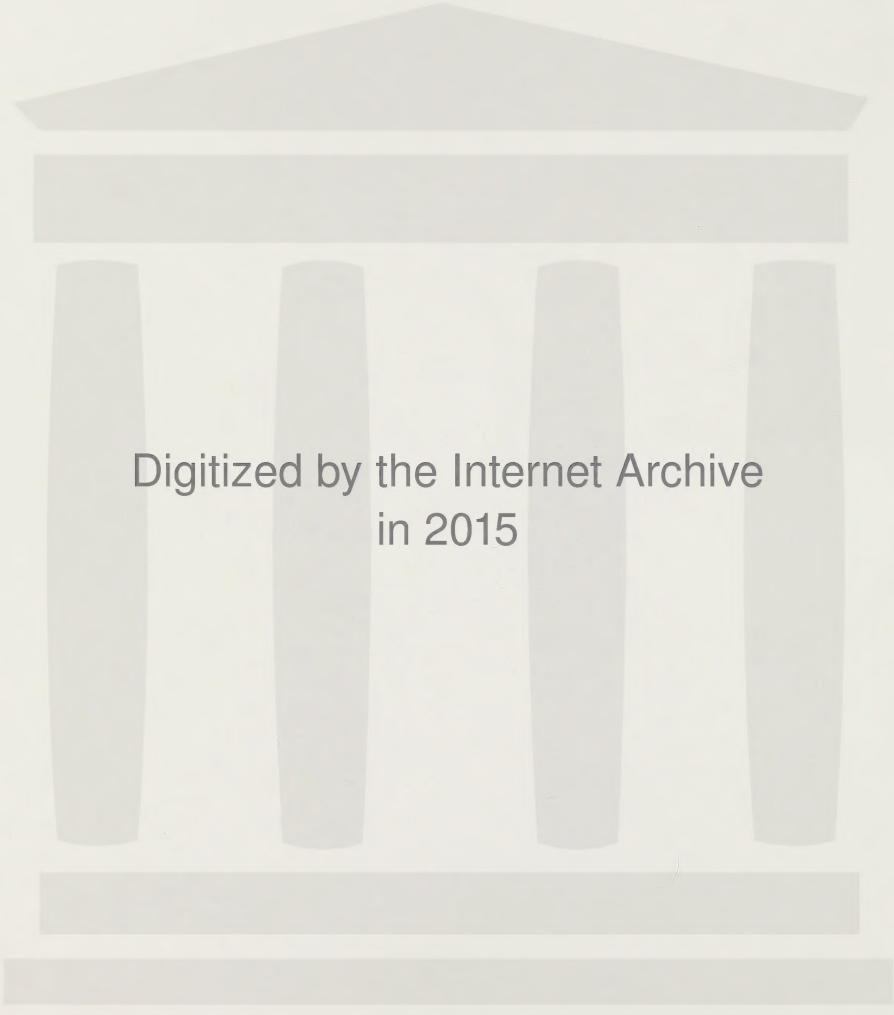
STABILIZATION/SOLIDIFICATION OF ORGANIC CONTAINING WASTES USING ORGANOPHILIC CLAY, COAL FLY ASH AND ORDINARY PORTLAND CEMENT

Alberta
ENVIRONMENTAL CENTRE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STABILIZATION/SOLIDIFICATION OF ORGANIC CONTAINING WASTES USING ORGANOPHILIC CLAY, COAL FLY ASH AND ORDINARY PORTLAND CEMENT

CANADIANA
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ABSTRACT

A study conducted at the Alberta Environmental Centre, cofunded by the Hazardous Substance Management Research Centre (New Jersey), examined the utility of specially treated bentonite clays for organic waste treatment. Bentonite clays exchanged with quaternary ammonium compounds adsorbed pentachlorophenol and 2,4,6-trichlorophenol in proportion to the chain length of the alkyl substituents on the quaternary ammonium compounds. Adsorption on to the modified bentonites could be described by the Langmuir and Freundlich models. Treatment formulae were optimized to minimize treatment additives and utilize a waste fly ash while maintaining sufficient unconfined compressive strength. The treatment formulation chosen for evaluation, Hexadecyl trimethylammonium-Bentonite/Ordinary Portland Cement and Fly Ash, successfully treated a surrogate waste containing 1300 mg PCP/kg waste, yielding a modified Toxicity Characteristics Leaching Procedure leachant of 29 ± 10 µgPCP/L. Metal containment by the cementitious components was unaffected by the presence of the modified clay.

INTRODUCTION

The safe treatment and disposal of hazardous wastes has become an area of concern for industry, government and the general public. Wastes disposed without treatment, utilizing land-based disposal scenarios (landfills and *in situ*), may seriously affect local ground-water quality.

The various physical and chemical characteristics of the wastes destined for land-based disposal must be considered for their environmental implications. Wastes containing free liquids are undesirable because they are immediately mobile and percolate through the receiving waste body, leaching metals and organics. The chemical contaminants may be in a readily soluble and mobile form such as the chloride or sulphate salts of metals which are readily leached and may be transported far from the waste site. Wastes may be subject to leaching by free liquid, (as above), incident precipitation and biological activity. Liquids may also degrade the physical integrity of solid wastes. This decrease in particle site increases the surface area available for leaching.

Stabilization/Solidification processes have been used to treat hazardous wastes to reduce the environmental impact of their disposal. Solidification processes remove free aqueous liquids usually by the hydration reactions of lime, cementitious materials such as ordinary Portland cement (OPC), or pozzolanic materials such as fly ash (FA) produced from pulverized coal combustion. Solidification may also yield a monolithic solid of reduced surface area, compared to the original waste. Stabilization processes using lime, cementitious and pozzolanic materials reduce the solubility of metal wastes by the precipitation of less soluble metal hydroxides (1) or metal incorporation and substitution reactions (2) into the hydration products of cement.

Treatment of inorganic wastes by stabilization/solidification techniques is common practice. However, organic waste stabilization/solidification is not well documented and a fundamental understanding of the mechanisms does not exist (3). Beneficial chemical interactions between organic wastes and cementitious treatment agents are limited. Connor (1) suggests that the chemistry of interaction is limited to oxidation, reduction, hydrolysis and salt formation. Adsorption, which is a function of available surface area, may also play a role in

organic containment, especially when organic wastes are finely dispersed. Few documented studies on treatment exist and the nature of chemical bonds formed during stabilization processes have not been studied (3).

Research into the interactions between organic wastes and ASTM Type I Portland cement has revealed that morphological changes occur to the organic containing cement (4 - 6). Ethylene glycol and *p*-bromophenol were found to cause changes in the crystallinity of calcium silica hydrate (CSH) formed during cement hydration (6). At high ratios of ethylene glycol to cement, changes in morphology were apparent and the incorporated organic was easier to extract.

In addition to the short-term interactions between organics and cement-based treatment processes, concerns have been expressed that over the long term, organic wastes may become mobile in the environment from pH effects, surface tension and biological degradation of fixation agents and contaminants (7).

A large number of commercial stabilization/solidification treatment technologies exist. However, for organic wastes, classical stabilization/solidification offers generally poor performance. An evaluation of 15 industrial stabilization/solidification treatment processes undertaken by Environment Canada, the United States Environmental Protection Agency and Alberta Environment (8) showed that organic contaminants are poorly contained even at relatively low concentration. The stabilization/solidification treatments evaluated were mainly cementitious and pozzolanic in nature. The study concluded that the development of stabilization/solidification processes for organic wastes are essential before they may be applied to complex wastes and site remediation. Otherwise, pretreatment of wastes containing even small amounts of organics would be required.

This publication will report on the use of specially modified clays as stabilization agents. Clays are naturally occurring alumino-silicate materials which have a variety of waste management uses. Various types of clay have been used as landfill liners and stabilization/solidification agents. Of particular interest are the smectites which are 2:1 clay minerals consisting of two tetrahedral layers and one octahedral layer. Substitution by elements

of different charge in the clay structure requires charge compensation. This is achieved by Na or Ca inclusion in the interlamellar aqueous layers (see Figure 1). These cations are loosely held, exchangeable in stoichiometric amounts and measured as the cation exchange capacity. Smectites expand when saturated with water and hence they have been used extensively as landfill liners.

The unique swelling and cation-exchange properties of smectite clays have suggested other uses. They have been proposed as agents for water and wastewater treatment (9, 10) after undergoing cation exchange with quaternary ammonium compounds.

The modification of such smectites as montmorillonite and bentonite clays by cation exchange with quaternary ammonium compounds has been studied extensively over the years (10, 11, 12, 13). Recently, researchers have considered the use of modified clays as a stabilization/solidification technique (13).

Researchers have found that exchanging interlamellar cations with larger quaternary ammonium compounds increased the basal spacing of the clay. McBride and Mortland (12) found that the basal spacing of ethylammonium smectite increased as a function of the proportion exchanged with tetra-*n*-propyl ammonium ion. Quaternary ammonium compounds behave as "pillaring agents" exposing interlamellar surfaces and increasing the effective surface area for adsorption.

The interlamellar spaces which are normally aqueous and hydrophilic may be changed to a more hydrophobic environment by the substitution of long chain alkyl groups or aromatic groups on the quaternary ammonium compounds (10, 13, 14).

McBride and Pinnavia (10) found that phenol was adsorbed to a greater extent by tetramethylammonium smectite rather than hexadecyltrimethylammonium (HDTMA) smectite.

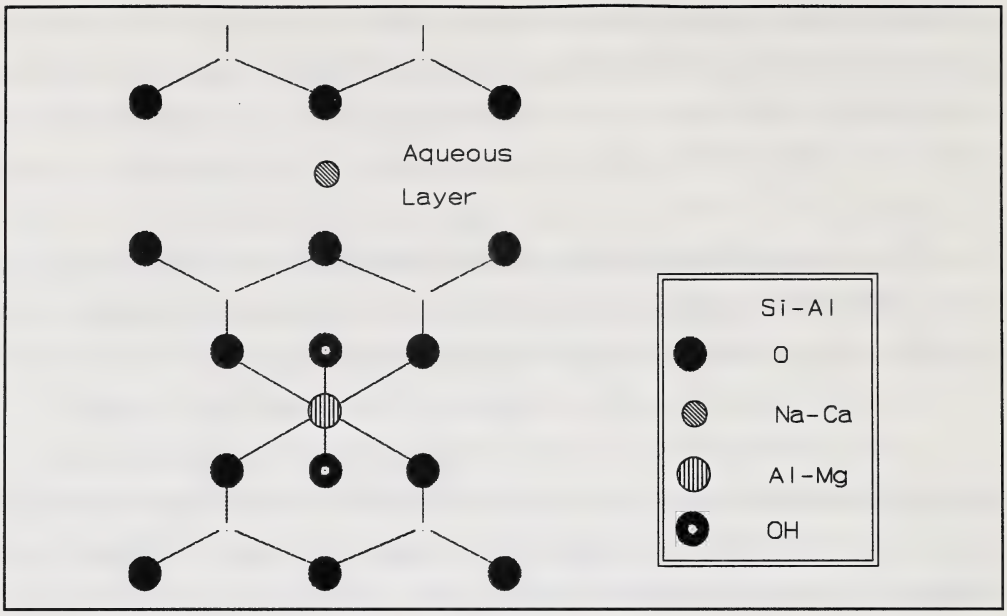


Figure 1. Diagram of Montmorillonite Showing Layer Structure and Exchangable Cations

Sheriff *et al.* (13) and Mortland *et al.* (14) compared the adsorption of phenol and chlorophenols on smectite clays treated with quaternary ammonium compounds with differing substituents and hence differing hydrophobicity. The efficiency of adsorption was quite different between compounds and treatments. Both authors were able to explain their results in terms of a relationship between the adsorbate and treatment compound hydrophobicity. Mortland *et al.* (14) showed by the level of adsorption and increased basal spacing, that trichlorophenol had penetrated interlamellar surfaces of HDTMA clay.

Clay-organic complexes have been studied by soil scientists among others, and a variety of interactions have been proposed (15). Of particular interest to the subject of alkyl ammonium treated clays is the work of Fenn and Mortland (16) who showed that phenol was adsorbed on tetramethylammonium montmorillonite by an ion-dipole interaction as well as by possible hydrogen bonding and π electron interaction with the silicate structure of the clay.

As mentioned previously, cementitious and pozzolanic stabilization/solidification agents have limited ability to treat organic containing wastes. However, they are well suited to treat inorganic wastes by the production of monolithic wastes with reduced surface area and permeability. As a final treatment for clay-organic stabilized wastes or mixed organic and metallic wastes, cementitious and pozzolanic (eg. fly ash) treatment processes have much merit.

Ordinary Portland cement is the basis of many commercial stabilization/solidification treatment processes (1). The hydration reactions of the calcium silicate portions of cement produce a highly alkaline environment due to $Ca(OH)_2$ production as is shown by the reactions of alite and belite below (17):

$$2\ (3\ CaO \cdot SiO_2) + 6\ H_2O \rightarrow 3\ CaO \cdot 2\ SiO_2 \cdot 3\ H_2O + 3\ Ca(OH)_2$$

$$2\ (2\ CaO \cdot SiO_2) + 4\ H_2O \rightarrow 3\ CaO \cdot 2\ SiO_2 \cdot 3\ H_2O + Ca(OH)_2$$

Fly ash is produced in large quantities from the combustion of pulverized coal and consists of spherical particles of variable silica, alumina and iron oxide contents. Fly ash is formed during the burnout of coal particles. Agglomeration of molten ash followed by fracturing of the particles during final burnout produces the larger sized fractions of 0.1 - 50 micron size. The smaller portions of fly ash are produced by the vaporization and subsequent condensation of alkali-metal salts, heavy metals and silica (18).

Aluminosilicate fly ashes with low CaO contents are (typically) Class F fly ashes which are pozzolanic in nature. A major phase is mullite ($3\ Al_2O_3 \bullet 2\ SiO_2$).

Fly ashes with higher CaO content, have cementitious properties and are classified as Class C flyash. Typical phases are anorthite ($CaO \bullet Al_2O_3 \bullet 2\ SiO_2$) and gehlenite ($2\ CaO \bullet Al_2O_3 \bullet SiO_2$).

The silicate phases of fly ash are capable of reaction with the $Ca(OH)_2$ formed during cement hydration. Reaction with the calcium aluminate phases of cement is also possible forming ettringite. These are beneficial reactions in concrete forming a less permeable material with enhanced sulphate resistance and lowered water requirements (18).

Fly ash may also contain a portion of adsorbed organic material such as polycyclic aromatic hydrocarbons and inclusions of incompletely oxidized coal.

The organic portion of coal fly ash may have its own beneficial properties as a treatment for organic containing wastes. Fly ashes are capable of adsorbing aromatic hydrocarbons (19). In a study by Liskowitz *et al.* (20), organic removal from an ash pond effluent, measured as chemical oxygen demand, was correlated with the carbon content of fly ash. Organic removal by flyash is beyond the scope of this study, and in any case its effect is likely small compared to that of organophilic clays.

The potential beneficial characteristics mentioned above, but mainly reduced treatment cost, makes the blending of ordinary Portland cement and fly ash an attractive option for a stabilization/solidification treatment process. Only a portion of the fly ash produced by coal combustion is used in cement manufacture and thus the utilization of this waste material will reduce its disposal requirements.

In this study, results of a joint effort undertaken by the Alberta Environmental Centre and the New Jersey Institute of Technology to improve the application of stabilization/solidification technology to organic containing wastes is reported. The studies performed at the Alberta Environmental Centre had the following objectives:

1) Evaluate the relative efficiencies of specially modified clays to stabilize organics;
2) Develop treatment formulae for the stabilization/solidification agents which maximize the utilization of coal fly ash, a waste product, while maintaining desirable engineering properties;
3) Test the above treatment formula's ability to effectively stabilize/solidify a surrogate industrial waste spiked with pentachlorophenol.

MATERIALS AND METHODS

Clay Treatment

The following materials were used to produce the organophilic clays used in this study.

1) Coarse Grade Wyoming Bentonite (NL Baroid Industries)
2) Sodium Chloride (Fisher Scientific Certified ACS Grade)
3) Tetramethylammonium Chloride (Fisher Scientific Reagent Grade)
4) Cetylpyridinium Chloride (Sigma Chemical Company)
5) Hexadecyltrimethylammonium Bromide (Sigma Chemical Company)
6) Methanol (pesticide grade Caledon Laboratories Ltd. Sodium Exchange)

Coarse Grade Wyoming Bentonite was ground to pass a 75 micron screen. Ten gram portions of ground clay were cation exchanged by treating with 100 mL portions of 1.0 M NaCl solution and mixing on a rotary extractor (25 rpm) for 24 hours. The suspensions were centrifuged for five minutes at 5000 G using a Dupont Instruments Sorvall RC-5B Refrigerated Super Speed Centrifuge and the supernatant discarded. The NaCl treatment was repeated as above.

Quaternary Ammonium Exchange

Portions of the sodium exchanged bentonite (Na-bentonite) produced by the above procedure were further treated with the quaternary ammonium compounds listed above in the following manner. Individual ten gram portions were exchanged with 1.0 M tetramethylammonium chloride (TMA) in distilled water, 0.25 M cetylpyridinium chloride (CP) in distilled water and 0.14 M hexadecyltrimethylammonium bromide in 20% methanol/80% distilled water in a manner similar to that used to produce Na-bentonite. The treated clays (TMA-bentonite, CP-bentonite and HDTMA-bentonite) were rinsed at least three times with the appropriate solvent (distilled water or 20% methanol/80% distilled water) in the same manner as the cation exchange was performed.

The treated clays were dried at 60°C, reground to pass a 75 micron sieve, and stored in sealed plastic containers.

Adsorption Studies

The following materials were used to study the partitioning of organics between solvent and solid (clay) phases.

1) Pentachlorophenol (Neat, Supelco Ltd.)
2) 2,4,6-Trichlorophenol (Neat, Supelco Ltd.)
3) Acetic Anhydride (ACS grade, BDH Chemicals)
4) 1,4-Dibromobenzene (99%, Aldrich Chemical Company Ltd.)
5) Potassium Carbonate (Reagent Grade, BDH Chemicals)
6) Hexane (Pesticide Grade, Caledon Laboratories Ltd.)
7) Methanol (Pesticide Grade, Caledon Laboratories Ltd.)
8) Dichloromethane (Pesticide Grade, Caledon Laboratories Ltd.)

All glassware used was thoroughly washed with laboratory detergent (Sparkleen - Fisher Scientific Ltd) and rinsed with tap water. This was followed by triple rinsing with the following solvents respectively: 5% nitric acid, (prepared from reagent grade nitric acid - BDH Chemicals), ASTM type I water and finally methanol. Glassware used in preparing analytical dilutions was further rinsed with hexane.

A 1000 ppm stock solution of 2,4,6-trichlorophenol or pentachlorophenol was prepared by adding 0.2500 g of neat compound to a 250 mL volumetric flask, dissolving and diluting to volume with methanol. From this stock solution, working standards of variable concentrations were prepared by pipetting different volumes of the stock solution into 100 mL volumetric flasks (see Table 1). Methanol was added to the flasks to establish a 10% or 50% solution, with ASTM type I water for 2,4,6-trichlorophenol and pentachlorophenol respectively.

Each standard was divided further into two corex centrifuge tubes, at 50 mL each. One tube was used as a standard, while the other had weighed portions of one of the different types of treated bentonite clays added.

The tubes were placed on a rotary extractor at 30 rpm for a period of 16 hours. The samples were removed from the extractor, transferred to 15 mL centrifuge tubes, and centrifuged at 10000 G for five minutes.

The following acetylation procedure is based upon that of Abrahamsson (21) with sample sizes modified to obtain good analyte recovery (>80%) by ensuring surplus acetylation reagent.

Appropriate volumes of sample were added to 70 mL of 0.1 M potassium carbonate prerinsed with dichloromethane (see Table 1). Acetic anhydride (0.5 mL) was added and vigorously stirred for four minutes. Approximately 8 mL of hexane was then added and the mixture stirred for a further three minutes. The solution was removed from the stirrer and upon settling the top layer was carefully decanted and transferred to a 25 mL volumetric flask. The solution was returned to the stirrer and the addition of hexane was repeated two additional times. The samples were then diluted to volume. Upon completion of the acetylation procedure, the samples were diluted appropriately to achieve the final desired concentration (see Table 1).

The samples were prepared for the gas chromatograph by adding 1 mL of sample to the sample vial along with an internal standard of 1,4-dibromobenzene (10 µL of a 50 ppm solution). This standard was used to verify the reliability of the results from the gas chromatograph (see Table 2 for operational parameters). A sample injection of 1 µL was used. The total instrument analysis time was 12.33 minutes.

Table 1. Sample Preparation

SAMPLE TYPE	VOLUME STOCK SOLUTION DILUTED (mL)	SAMPLE CONC. (ppm)	SAMPLE VOLUME FOR ACETYLA-TION	ACETYLATED VOLUME	ANALYTICAL DILUTION FACTOR	FINAL CONC.* (ppm)
STANDARD	1.0	10.0	5.0	25.0	2.0	1.0
STANDARD	2.0	20.0	2.0	25.0	2.0	0.8
STANDARD	5.0	50.0	1.0	25.0	2.0	1.0
STANDARD	7.0	70.0	1.0	25.0	2.0	1.4
STANDARD	10.0	100.0	1.0	25.0	5.0	0.8
CLAY SAMPLES	1.0	10.0	5.0	25.0	1.0	2.0
CLAY SAMPLES	2.0	20.0	5.0	25.0	1.0	4.0
CLAY SAMPLES	5.0	50.0	5.0	25.0	2.0	5.0
CLAY SAMPLES	7.0	70.0	1.0	25.0	2.0	1.0
CLAY SAMPLES	10.0	100.0	1.0	25.0	5.0	2.0

*Assuming no sample effect or losses

Table 2. Gas Chromatograph Operational Parameters

GAS CHROMATOGRAPH:	Varian 3400
INJECTOR:	Varian 1077 Splitless Injector temp: 270°C
COLUMN:	25m x 32mm x 52µm film: HP-5 crosslinked phenyl-methyl silicon with a 20cm guard column of deactivated fused silica tubing.
DETECTOR:	^{63}Ni Electron Capture Detector temp: 310°C
CARRIER:	Flow rate 5.03mL/min helium gas Make-up gas 23.3 mL/min nitrogen
TEMPERATURE PROGRAM:	Initial column temp: 60°C Initial column hold time: 1 min. Final column temp: 230°C Temp. rate: 15°C/min.

Physical Testing

The materials used to produce the stabilized/solidified wastes for physical testing and waste fly ash optimization follow.

1) ASTM Type I Portland cement (Canada Cement Lafarge)
2) Fly Ash (Classified, Class F, Western Canada Fly Ash)
3) Motor Oil (SAE #10 W30, Petro Canada Ltd.)
4) TMA - bentonite (produced above)
5) Tap Water (North Saskatchewan River, typical finished water pH 8.5, 100 ppm total hardness)
6) Steel Mill Baghouse Dust

Steel Mill baghouse dust containing a variety of heavy metals was mixed with a portion of motor oil and used as a model waste. Various combinations of model waste, treated clay, ordinary Portland cement (OPC) and classified Western Canada fly ash (FA) (see Table 3) were tested for unconfined compressive strength according to ASTM C109-87. Samples were cured at 23°C and 98% relative humidity for 28 days before testing.

Leaching Tests

The optimal treatment formulation (without motor oil) was tested for its ability to retain pentachlorophenol by subjecting the cured treated waste to a modified Toxicity Characteristic Leaching Procedure (TCLP) (22).

One hundred and fifty-five gram portions of steel mill baghouse dust were spiked with pentachlorophenol (10,000 mg/L in methanol) to yield a surrogate waste containing approximately 1300 mg/kg of pentachlorophenol. Sufficient tap water was added to produce a waste slurry. (Note: additional water, equivalent to 6% of the final mixture, was required. This was compensated for by slightly lowering the overall percentage of steel mill baghouse dust to 57%.

Table 3. Physical Test Formulations

Baghouse Dust (%)	Motor Oil (%)	Portland Cement (%)	Classified Fly Ash (%)	TMA Treated Clay (%)	Water (%)	Sample No.
62.0	1.9	5.2	10.3	---	20.7	1
62.5	1.9	5.2	10.4	0.8	19.3	2
62.5	1.9	5.2	10.3	1.5	19.1	3
62.4	1.9	3.1	12.5	---	20.2	4
62.5	1.9	3.1	12.5	0.8	19.3	5
62.5	1.9	3.1	12.4	1.5	19.1	6
63.0	1.9	1.0	14.7	---	19.4	7
61.2	1.8	1.0	14.3	0.8	20.9	8
61.0	1.8	1.0	14.2	1.5	20.3	9

Ordinary Portland cement, fly ash and modified clay additions were kept at the same level as [sample 9] in PHYSICAL TESTING.)

HDTMA bentonite was added to the waste slurry, mixed well and stored in a humidity chamber at 23°C, 98% relative humidity for 16 hours before the addition of ordinary Portland cement and fly ash. The stabilization/solidification agents were mixed in by hand and the samples were allowed to cure for 28 days at 23°C and 98% relative humidity. Four sample preparations were tested:

1) spiked surrogate waste;
2) spiked surrogate waste, ordinary Portland cement and fly ash;
3) spiked surrogate waste, ordinary Portland cement, fly ash and untreated clay (Na-bentonite);
4) spiked surrogate waste, ordinary Portland cement, fly ash, treated clay (HDTMA - bentonite).

All samples were prepared in triplicate by blocking with respect to time (ie. the four trials, one of each sample formulation, were prepared on each of three different days).

Upon the completion of curing the samples were crushed according to the TCLP. The leachant used was ASTM Type I water to ensure an alkaline pH which is more aggressive on phenolics than the acidic leachants used in the TCLP (phenates are more soluble than phenols). All other features of the Toxicity Characteristic Leaching Procedure were followed. Filtered leachates were analyzed for pentachlorophenol as above. PCP surrogate spikes of sample 4 leachate yielded an analytical recovery of 102 ± 5%.

Portions of the stabilized/solidified wastes were also subjected to TCLP testing to evaluate metal fixation. Fifty gram sample portions were tested using TCLP extraction fluid #2 (0.1 N acetic acid). Metal analysis on the TCLP extracts were performed using a sequential Jobin-Yvon 38 inductively coupled plasma emission spectrophotometer.

RESULTS AND DISCUSSION

Physical Testing

The test formulations for physical testing show that (Table 3) waste, additive (OPC, FA), and water ratios were held constant (to within a RSD of 1% for baghouse dust, 1% for additive and 3.6% for water due to varying clay proportions). OPC/FA ratios were varied between 0.07, 0.25 and 0.50 corresponding to 1.0, 3.1, and 5.2% OPC respectively. Clay treated with tetramethyammonium chloride was added in proportions of 0%, 0.8%, and 1.5%.

Unconfined compressive strength data is summarized in Table 4.

Table 4. Compressive Strength Data

Sample No.	Unconfined Compressive Strength (kPa)		
	Mean	Sx	No. of Tests
1	6212	---	1
2	8653	1351	3
3	10239	545	3
4	5281	152	3
5	5840	352	3
6	7060	207	3
7	1958	90	3
8	2055	186	3
9	1310	90	3

Analysis of Variance and Comparison of Treatment Means

OPC/FA Ratio

A model of unconfined compressive strength (UCS):

$$UCS = \mu + MTE + RE$$

where μ is the overall true mean (estimated by the grand mean of UCS), MTE are the mean treatment effects due to varying OPC content, and RE is random error; explained 90% ($p<0.05$) of the variation in UCS.

Mean comparison data are shown in Table 5. Means not showing a common letter are different at $\alpha = 0.05$ based on the Ryan-Einot-Gabriel-Welch (REGW) Multiple Range Test suitable for unequal sample sizes. The highest OPC content, 5.2%, is significantly different than the others and represents a 48% increase in UCS when compared to 3.1% OPC.

OPC/FA Ratio and Clay

Response at each of the 9 design points in the 3 x 3 factorial were fit to a second-degree polynomial by regression analysis. Ninety eight percent (98%) of the variation in UCS was accounted for by fitting this model ($P < 0.0001$).

The equation, with estimates of the intercept and five terms (significant terms are underlined; all underlined terms were significant at $P \leq 0.01$, or less) is as follows:

$$UCS[KPA] = -179.69 + \underline{2542.04(\%OPC)} - \underline{1270.02(\%Clay)} - \underline{259.86(\%OPC)^2} + 83.49(\%Clay)^2 + \underline{738.46(OPC*Clay)}$$

Most notable are the linear and quadratic effects of % OPC, followed by the increase in UCS due to increasing % Clay; the response surface of these relationships, illustrated by contour plots (Figure 2) is obvious. Figure 3 illustrates the significant OPC + Clay interaction term, which is readily apparent at 1% OPC content.

Table 5. OPC Mean Comparisons

OPC Level (%) (Treatment)	No. of Data	Mean (kPa)	Group
5.2	7	8984	A
3.1	9	6081	B
1.0	9	1772	C

Table 6. OPC and Clay Mean Comparisons

Treatment (%)		Mean (kPa)	Group
OPC	Clay		
5.2	1.55	10239	A
5.2	0.78	8653	B
3.1	1.55	7060	C
5.2	0	6212	C D
3.1	0.78	5840	C D
3.1	0	5281	D
1.0	0.78	2055	E
1.0	0	1958	E
1.0	1.55	1310	E

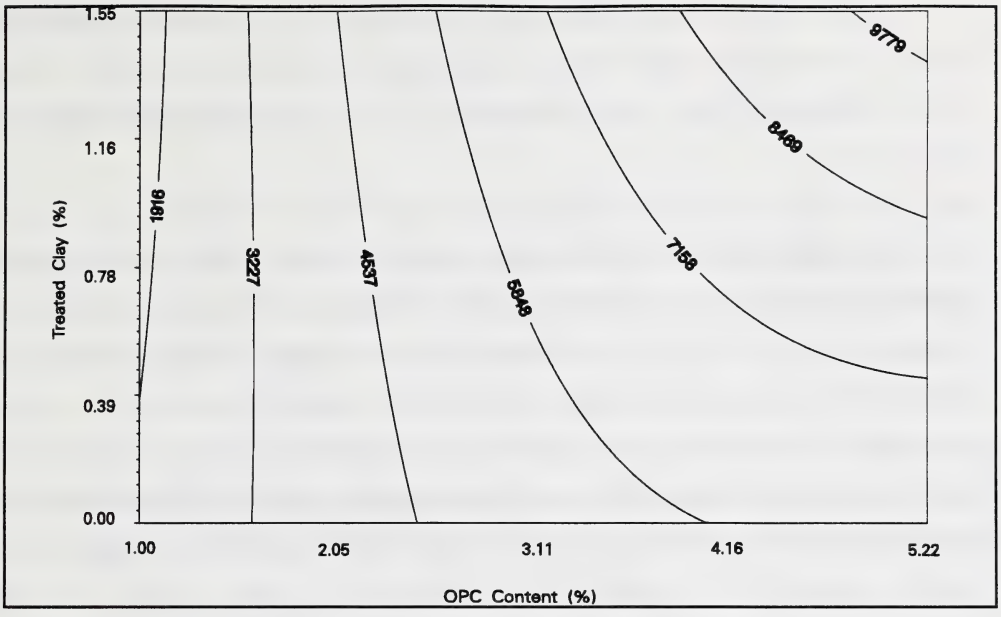


Figure 2. Contour Plot for UCS (kPa)

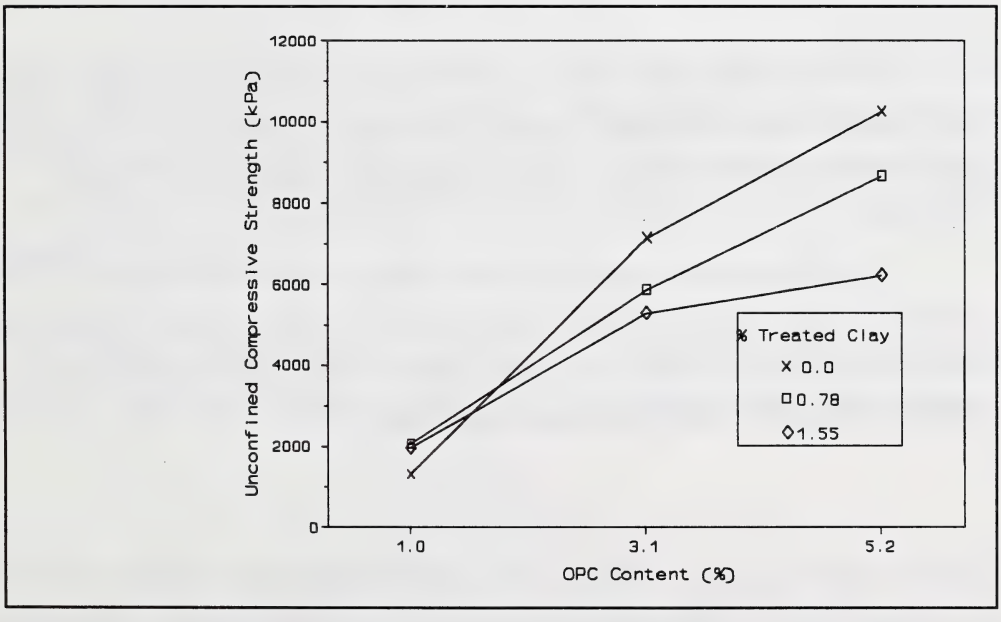


Figure 3. Effect of OPC Content on Unconfined Compressive Strength

Sample means, at each design point, were compared by the REGW multiple range test (Table 6). These results support the regression analyses, by confirming the OPC = 5.2 and Clay = 1.55 combination to be a region of increasing UCS, and maxima within our experimental design space.

For this Foundry Bag House Dust, small amounts of OPC are sufficient to yield significant unconfined compressive strength (UCS). In practice waste treatment operations strive to maintain 345-690 kPa UCS to ensure the support of heavy landfill spreading equipment. Increased UCS is generally associated with improved weathering characteristics. As one of the goals of our joint study is process development, an OPC/FA ratio of 0.07 was chosen to maximize fly ash utilization while maintaining desirable physical properties. Baghouse dust, consisting largely of iron oxides, a variety of heavy metals, and only trace organics, has minimal negative impacts on solidification/stabilization. Other wastes amenable to solidification/stabilization will need higher OPC/FA ratios or higher additive/waste ratios depending on applicable landfill costs and the solids content of the wastes.

Sheriff(13) reports that the UCS of cement mixed with treated clays (HDTMA and benzyldimethyltetradecylammonium chloride) was reduced slightly and that the adsorption of phenol further reduced the strength. The total decrease in strength was 5 - 15%.

The treatment chemical used in our study, TMA, is more hydrophillic than HDTMA and may have a different effect on the hydration and curing of cement. Actual industrial waste was incorporated in the test mixtures and these different results show the importance of testing specific treatments and wastes for disposal parameters.

ADSORPTION STUDIES

Pentachlorophenol/Clay Isotherms

Figure 4 summarizes the results of pentachlorophenol (PCP) adsorbed on the various treated clays versus the equilibrium solution concentration. TMA-bentonite and Na-bentonite do not adsorb PCP to any considerable extent. However, CP-bentonite and HDTMA-bentonite adsorb PCP to levels of 100 mg/g of treated clay and higher.

The shape of the CP-bentonite and HDTMA-bentonite isotherms is indicative of favourable adsorption. These isotherms were regressed according to the Langmuir and Freundlich models of adsorption. The Freundlich model describes adsorption by means of the following equation:

$$q = KC^{1/N}$$

where q is the amount of adsorbate per unit mass of adsorbent (moles/g or mg/g), K is an empirical constant related to the energy of adsorption, C is the equilibrium solution concentration (moles or mg/L), and N is an empirical constant (>1). The Freundlich isotherm assumes that the number of adsorption sites associated with a free energy of adsorption decreases exponentially with increasing free energy.

The Langmuir isotherm assumes that the energy of adsorption is the same for all adsorption sites regardless of the degree of coverage. The Langmuir isotherm takes the form:

$$q = \frac{Qbc}{(1 + bc)}$$

where Q is the maximum amount of adsorbate per unit adsorbent (moles/g or mg/g) forming a complete monolayer on the surface and b is an empirical constant (g/mole or g/mg) related to the energy of adsorption.

The Freundlich and Langmuir isotherms will agree over moderate ranges of concentration. However, the Freundlich isotherm does not approach linear adsorption at low concentrations or reach a limiting value at high concentrations, as the Langmuir isotherm does. Figures 5 to 8 display results for the CP-Bentonite and HDTMA-Bentonite regressions. Regressions are highly significant for both models ($p \leq 0.017$). The term R^2, which describes the variation explained by the independent variable for linear models, must be used with caution for non-linear models. An R^2 value from a non-linear regression is an estimate rather than an exact measure of explained variation. Discrimination between the models is difficult because of the few data points available at higher equilibrium values. However, for the HDTMA-Bentonite isotherm, the Langmuir regression appears most appropriate based on the analysis of residuals which appear independent and normally distributed, as well as the fact that the estimated parameters are less correlated (ie. more independent).

The results which show that PCP removal is a function of treatment compound can be explained by considering the nature of the bentonite clay and its quaternary ammonium cation exchanged forms.

Na-Bentonite (see Figure 1) consists of interlamellar layers that are aqueous in nature. PCP is largely unable to displace the water adsorbed on the mineral surface of the clay and hence PCP adsorption does not occur to any measurable extent at low equilibrium concentrations.

TMA (see Figure 9) contains methyl groups as substituents which do not apparently change the aqueous nature of the interlamellar spaces of the TMA-bentonite to any significant extent. Thus, TMA-bentonite is not a significantly better adsorbent of PCP than Na-Bentonite.

The hydrophobicity of the interlamellar spaces of treated bentonite clays has been demonstrated to be a controlling factor describing the adsorption of organic chemicals. Sheriff (8) showed that TMA treated clay which is relatively hydrophilic to be more efficient at removing phenol than 2,3-dichlorophenol from solution. HDTMA treated clay was more efficient at removing 2,3-dichlorophenol than phenol from solution.

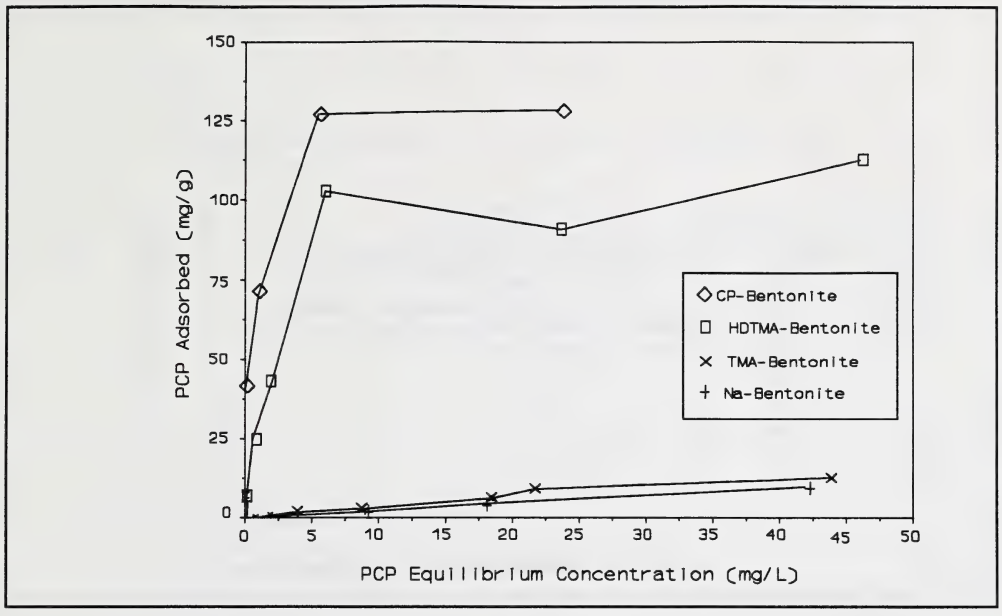


Figure 4. PCP/Clay Isotherms (23° C) from 50% Methanol/Water

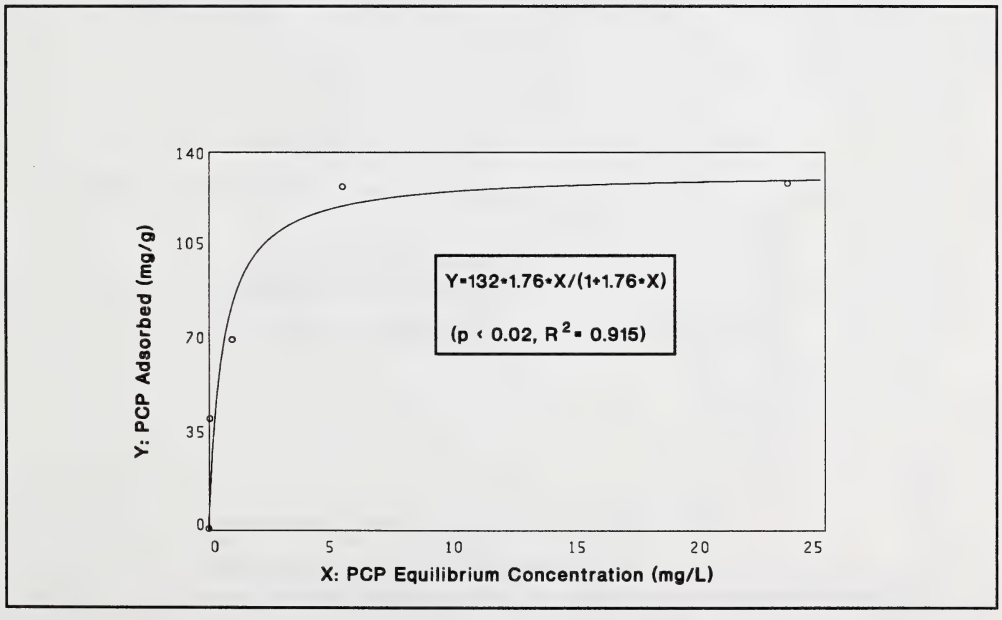


Figure 5. Langmuir Regression of PCP/CP-Bentonite Isotherm

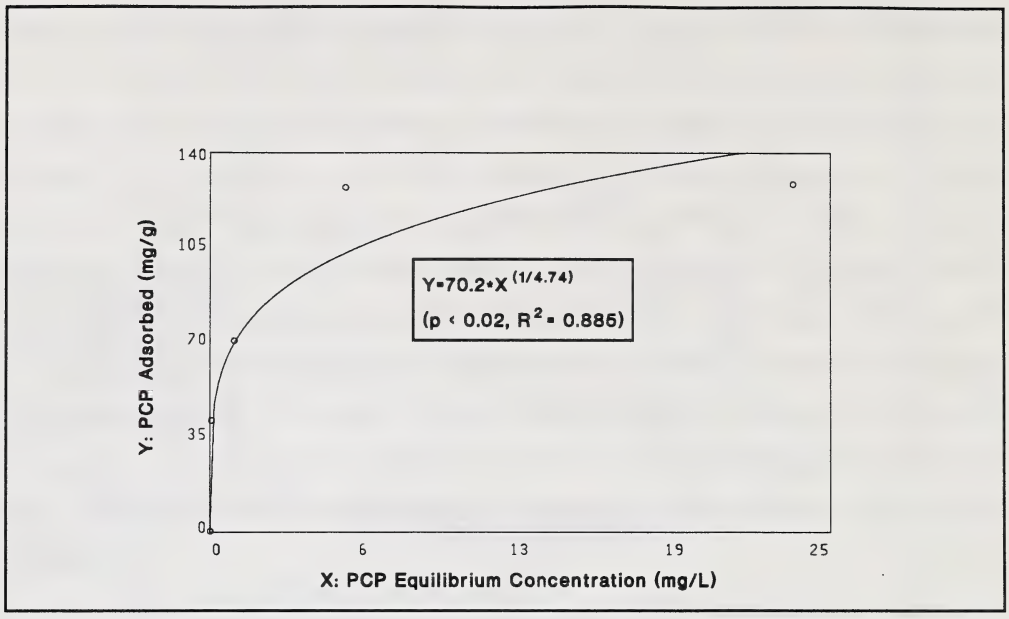


Figure 6. Freundlich Regression of PCP/CP-Bentonite Isotherm

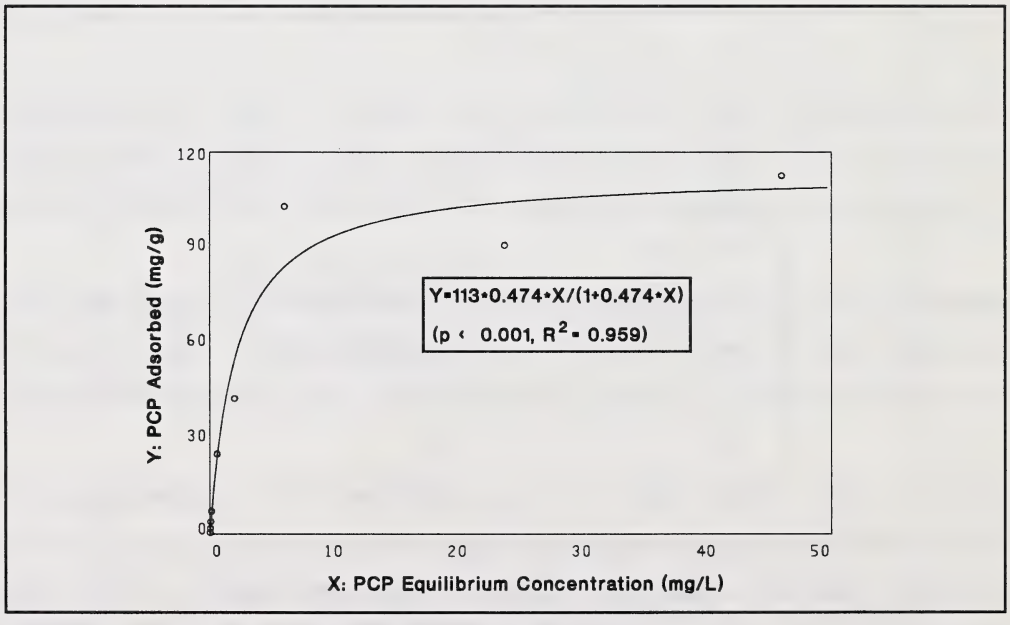


Figure 7. Langmuir Regression of PCP/HDTMA-Bentonite Isotherm

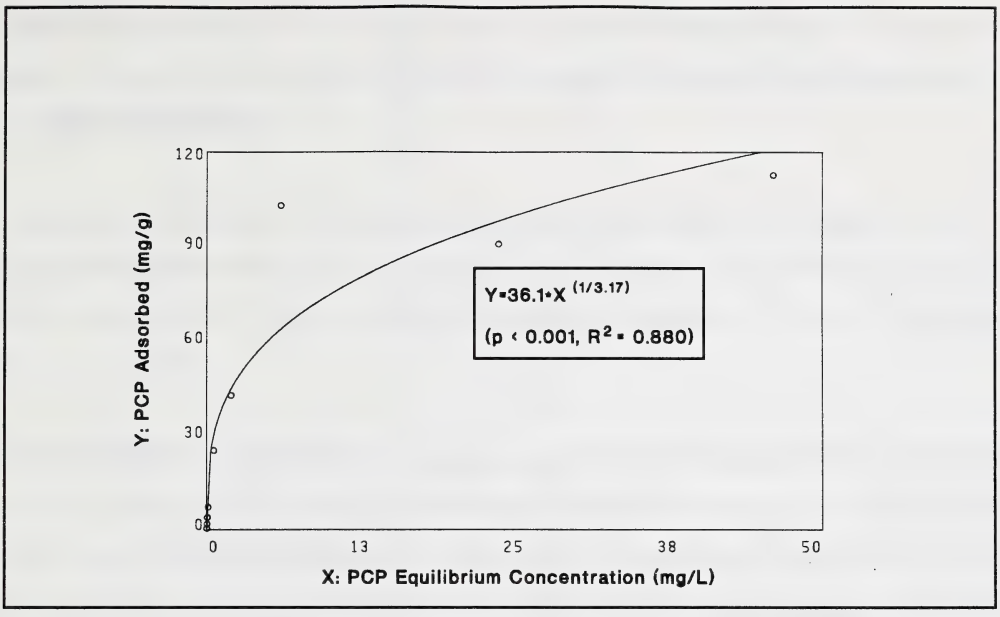
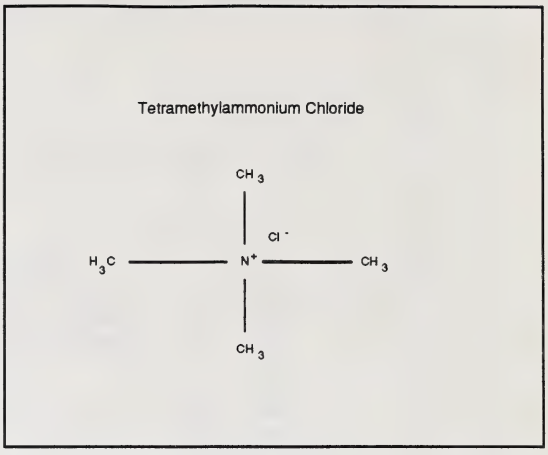
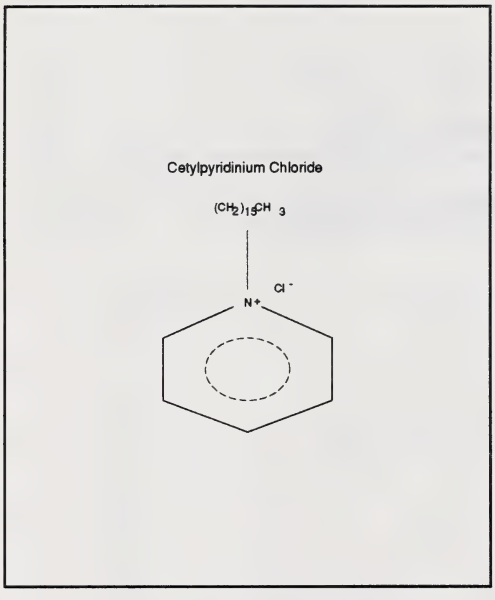


Figure 8. Freundlich Regression of PCP/HDTMA-Bentonite Isotherm





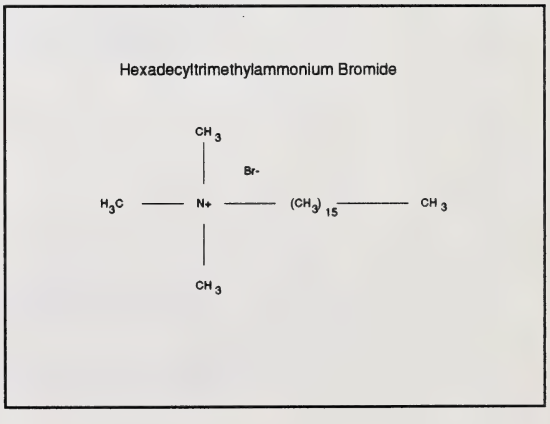


Figure 9. Quaternary Ammonium Compounds

HDTMA-Bentonite and CP-Bentonite with a long alkyl chain substituents (see Figure 9) are capable of obscuring the clay mineral surface from water and change the interlamellar spaces to a hydrophobic environment.

Boyd (23) *et al.* studied PCP sorption from water and measured the adsorbed PCP on HDTMA treated clay to be (equivalent to) 32 mg/g at an equilibrium concentration of 5.3 mg/L. Twenty-nine mg/g of PCP were adsorbed on hexadecylpyridinium (CP) clay at the same equilibrium concentration.

In this study 80 mg PCP/g clay were adsorbed on HDTMA-Bentonite at an equilibrium solution concentration of 5.3 mg PCP/L. CP-Bentonite was found to adsorb 119 mg PCP/g clay at an equilibrium solution concentration of 5.3 mg PCP/L. These estimates were made using the Langmuir regression equations. (If the Freundlich regression is used the results are 61 mg PCP/g HDTMA-Bentonite 100 mg PCP/g CP-Bentonite.) The clays used in the present study were cation exchanged with an excess of treatment compound while Boyd (23) used an amount equivalent to the cation exchange capacity. The treatment compounds may be adsorbed in excess of the clay's cation exchange capacity, by other adsorption-type processes, increasing its organic carbon content. This may explain the increased PCP adsorption.

Several authors suggest a partitioning between aqueous organic compounds and the organic content of adsorbents. Wilken (24) shows a relationship between hexachlorobenzene adsorption and organic carbon content on naturally occurring adsorbents. Schellenberg (25) states that the sorption of phenolate species is predominantly a partitioning process between the aqueous phase and the organic phase present in a natural sorbent. Boyd (23) extends this argument to HDTMA clays whose mineral surface is obscured by the large organic cation. Partition coefficients for the organic portion of the HDTMA clays were comparable to those for octanol/water. No competitive effect was noted between trichlorophenol and PCP for adsorptive sites. Isotherms of PCP and HDTMA clay at pH 5.5 and 10 were similar, suggesting that non-polar interactions were the chief mode of interaction between PCP and HDTMA clay.

Although researchers have found a variety of clay adsorbate interactions possible (15), the work presented here and by others suggests that the nature of the organo-cation molecules are important in determining the capacity of organophilic clays for organic pollutants.

Pentachlorophenol is a common contaminant from wood treatment operations. It is often found as a soil contaminant at orphaned wood treatment facility sites. Pentachlorophenol adsorption on soils is a reversible process (26) and so PCP is a potential groundwater contaminant. Boyd *et al.* (27) has suggested that HDTMA could be used as a soil modification agent and found that HDTMA is a more powerful partitioning agent than ordinary soil organic matter (28). There is clearly a potential for organophilic clays to be utilized for the site remediation of wood treatment facilities, to contain PCP and prevent its migration into groundwater supplies.

Trichlorophenol/Clay Isotherms

Figure 10 summarizes the results of TCP adsorbed on the various treated clays versus the equilibrium solution concentration. 2,4,6-Trichlorophenol (TCP) is more soluble in aqueous solutions than pentachlorophenol and thus these isotherms were generated using 10% methanol/90% water solutions. The results are somewhat similar to those observed for PCP (Figure 4) in that TCP is adsorbed to a significant extent by CP and HDTMA-Bentonite while TCP is not adsorbed to any significant extent by TMA or Na-Bentonite. The amount of TCP adsorbed appears smaller when measured on a mg/g basis. However, on a molar basis, the results are more similar. (Note that the molecular weight of PCP is 266.33 vs 197.45 for TCP.) The CP-Bentonite and HDTMA-Bentonite isotherms were regressed according to the Langmuir and Freundlich isotherms as before. Results are summarized in Figures 11 to 14. The Freundlich and Langmuir regressions appear to have equal utility in describing TCP adsorption on CP-Bentonite and HDTMA-Bentonite. TCP equilibrium concentrations were only studied up to 17 mg TCP/L and thus the adsorption of TCP may not have effected complete monolayer coverage.

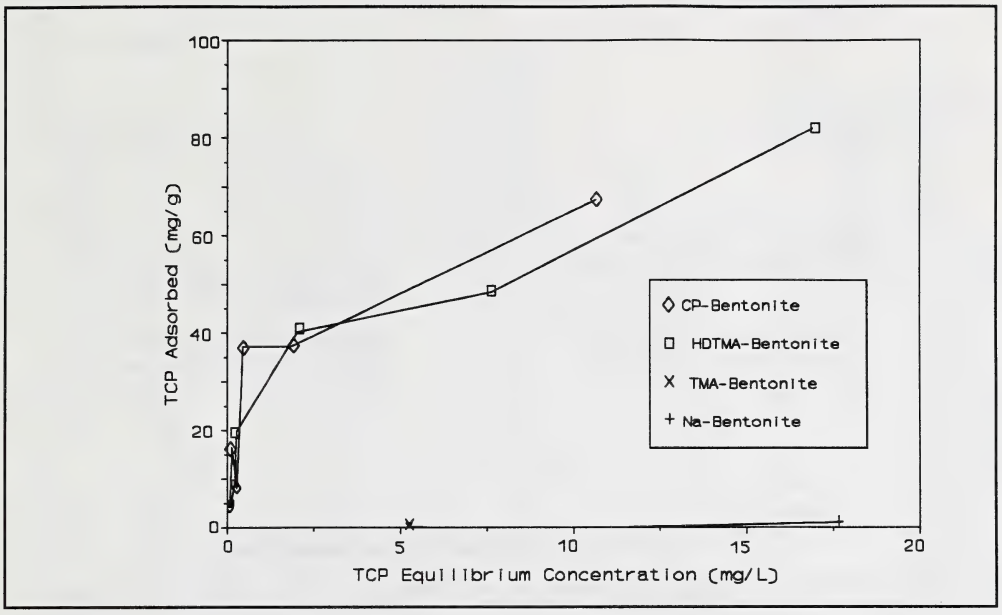


Figure 10. TCP/Clay Isotherms (23° C) from 10% Methanol/Water

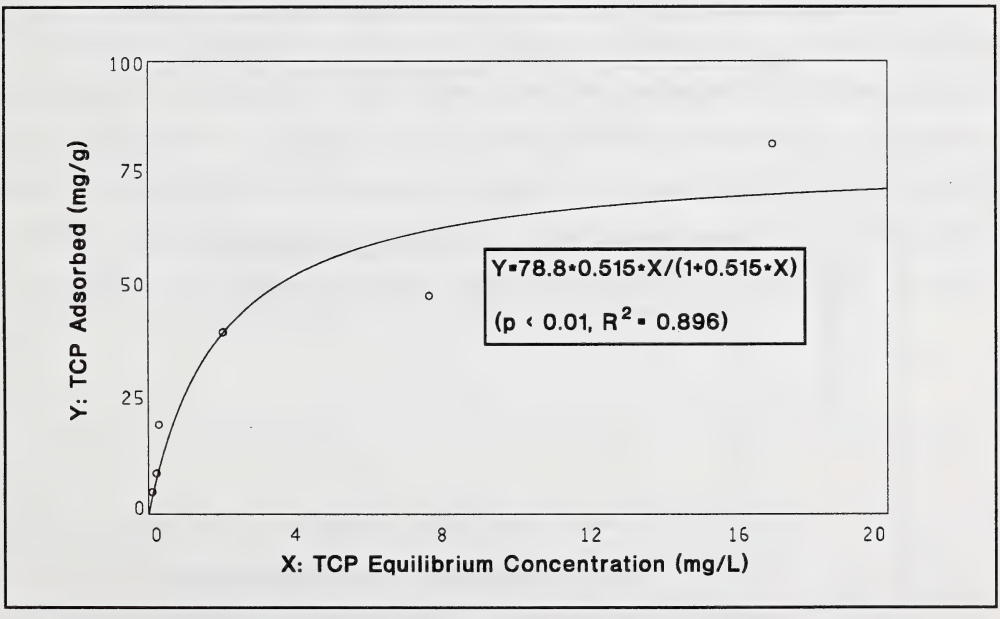


Figure 11. Langmuir Regression of TCP/HDTMA-Bentonite Isotherm

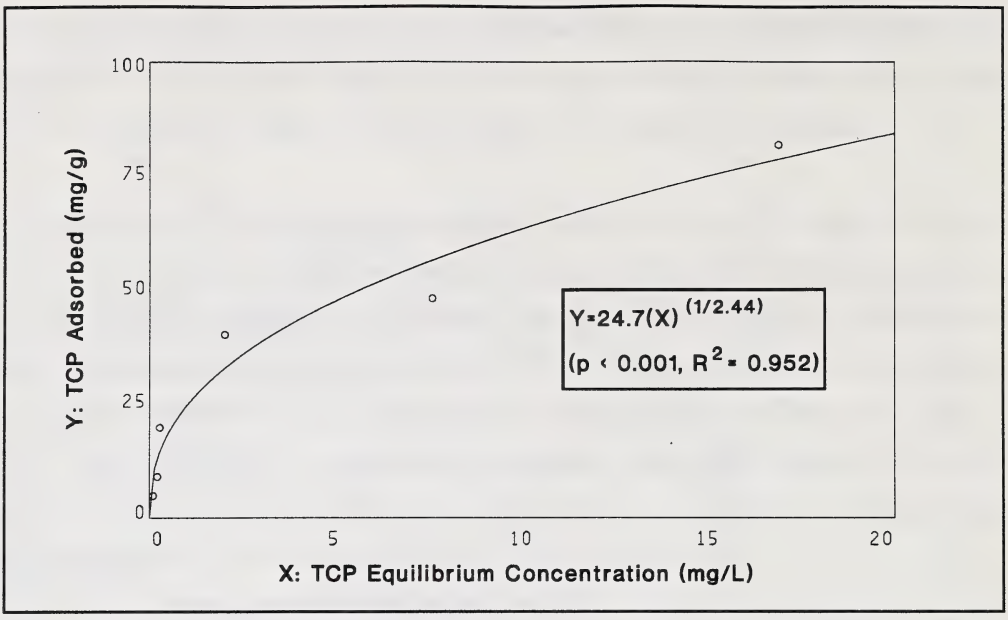


Figure 12. Freundlich Regression of TCP/HDTMA-Bentonite Isotherm

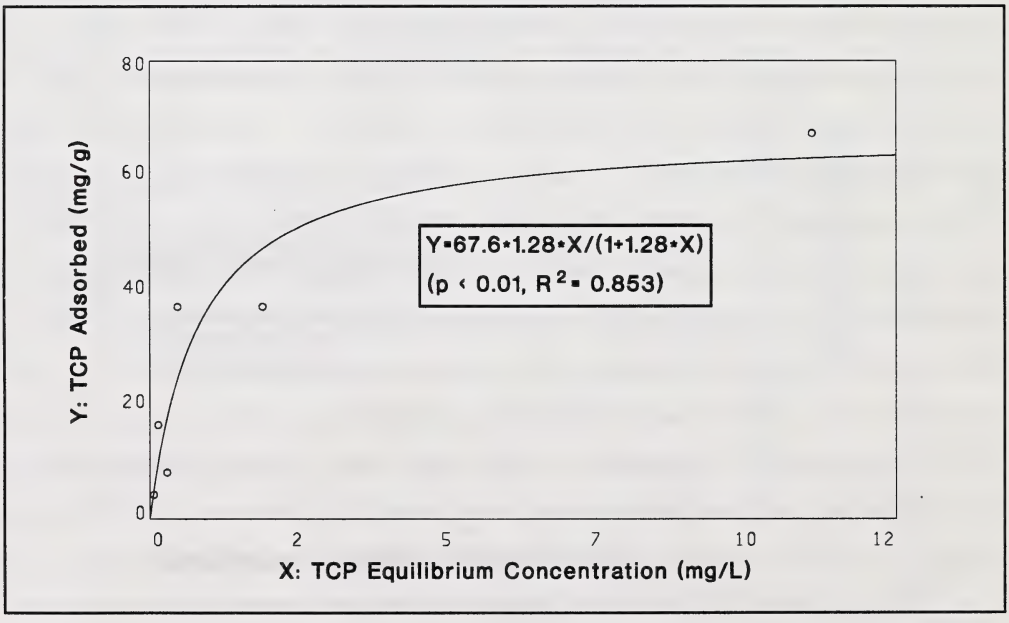


Figure 13. Langmuir Regression of TCP/CP-Bentonite Isotherm

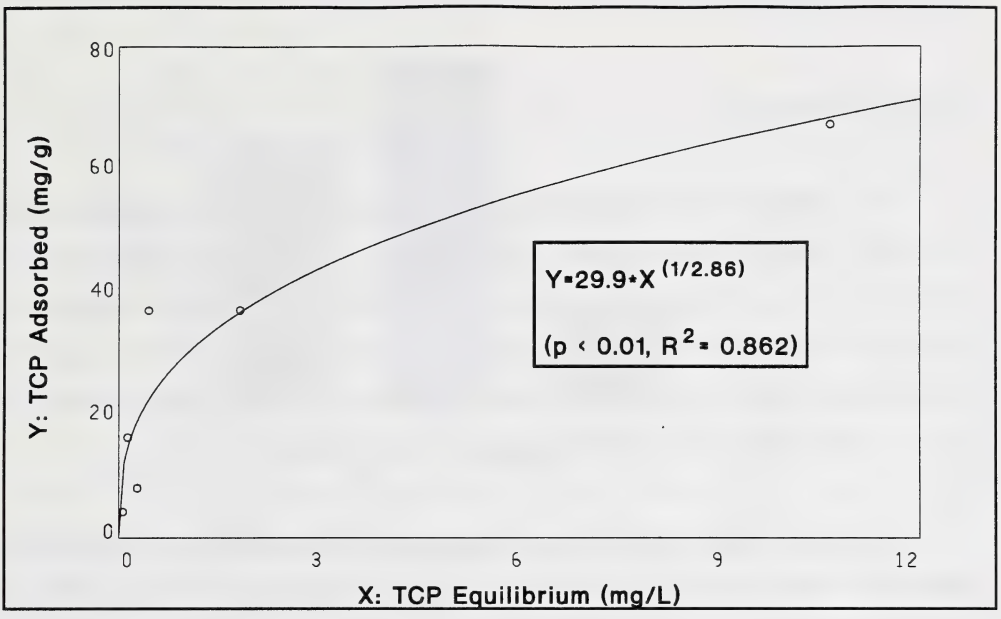


Figure 14. Freundlich Regression of TCP/CP-Bentonite Isotherm

To summarize the results from PCP and TCP adsorption isotherms, it has been shown that adsorption appears to be a function of alkyl chain length (and hydrophobicity) of the quaternary ammonium compound. In addition, the adsorption results obtained at low equilibrium concentration levels are effectively modelled by both the Langmuir and Freundlich isotherm models. Finally, the isotherm methods used above provide a useful means of evaluating various forms of quaternary ammonium compound exchanged bentonite for their ability to adsorb pollutants.

LEACHING TESTS

PCP Leachate Results

The isotherm studies described previously show that various quaternary ammonium compounds may be easily compared. But isotherms do not allow the prediction of real world behaviour or, for solubility limited compounds like chlorophenolics, their performance in standard regulatory tests which utilize aqueous leachants. The modified TCLP method (Canadian Extraction Procedure) used here was chosen to ensure an alkaline aqueous leaching environment which is more aggressive to phenolics than an acidic leachate.

Results for PCP (average of three tests) are summarized in Figure 15. If no matrix - PCP interactions were present, an approximate leachate concentration of 36 mg PCP/L would be theoretically recovered from the treated wastes (OPC/FA, OPC/FA + Na-Clay, OPC/FA + HDTMA-Clay), while 45 mg PCP/L would theoretically be extracted from the surrogate waste sample (foundry dust). The above concentrations are meant only to show the potential effect of sample dilution by treatment agents.

The foundry dust surrogate shows that only a fraction of the PCP was recoverable in an alkaline aqueous extraction. Only 19.6 mg PCP/L ± 2.0 mg PCP/L (standard error s.e.) was recovered which is only 44% of the theoretical amount.

A larger portion of PCP was extracted from the portion treated with OPC and FA (22.6 mg PCP/L ± 0.7 mg PCP/L s.e.), which is approximately 63% recovery. This higher recovery is likely due to the formation of Ca-phenate complexes which are highly soluble.

In comparing the three treated samples by two sample t-tests, both the cementitious treatment with Na-Bentonite, 6.92 mg PCP/L ± 0.75 mg PCP/L s.e., and cementitious treatment with HDTMA-Bentonite, 0.029 mg PCP/L ± 0.010 mg PCP/L, significantly reduced, $p < 0.001$, PCP leachate concentrations as compared to cementitious treatment alone. The HDTMA-

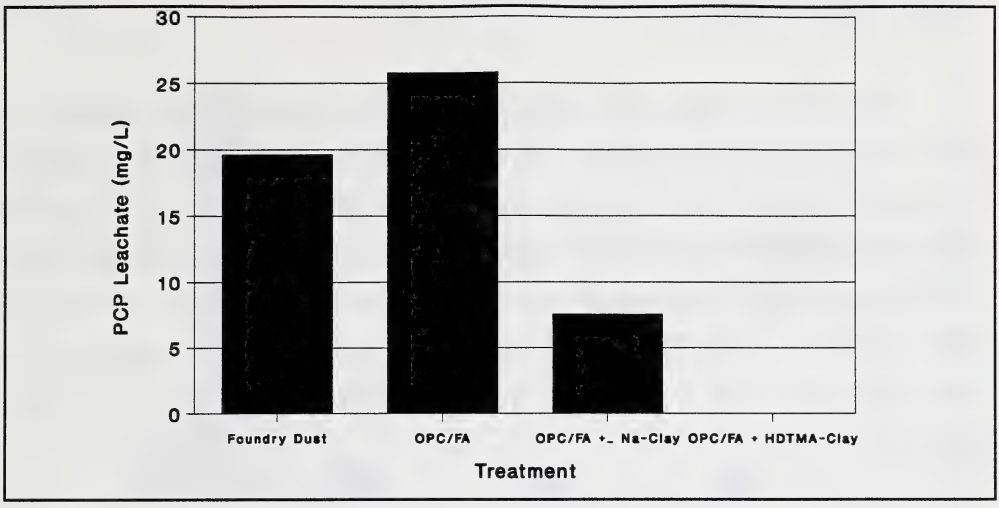


Figure 15. PCP Leachate Results Showing the Effect of Various Treatments

Bentonite treatment resulted in a significantly lower PCP leachate concentration than the Na-Bentonite treatment ($p < 0.001$). The treatment effects are summarized in Table 7.

Table 7. Treatment Effects

Treatment	Difference as mg PCP/L*	
	OPC/FA	Na-Bentonite
Na-Bentonite	18.59 ± 0.94	-----
HDTMA	25.77 ± 0.74	7.18 ± 0.64

* mean ± s.e.

Although a significant treatment effect is noted for Na-Bentonite as compared to the OPC/FA treatment, the HDTMA-Bentonite treatment was far superior. It generated a leachate concentration which approached Canadian drinking water guidelines (0.06 mg/L). Because of the various losses of organics and relatively mild leaching media in regulatory tests, isotherm equilibrium concentrations generated with methanol solutions are quite conservative and rigorous in their evaluation of organophilic clays.

Metal Leachate Results

TCLP (0.1 N acetic acid) results for Cr, Pb, and Zn are shown in Figure 16. Results show that the foundry dust contains a level of Pb which exceeds the TCLP regulatory level of 5 mg/L (22). Both Pb and Zn were reduced to their detection limits of 0.07 mg/L and 0.003 mg/L respectively by all three waste treatments. Chromium is significantly reduced ($p < 0.001$) by all three treatments. The Cr treatment effect can be explained solely by dilution effects. (The waste loading was only 57% of the total treated waste.) This suggests that Cr is in the hexavelant state which is unaffected by cementitious waste treatments and thus requires pretreatment.

The utility of cementitious treatments in the stabilization and effective treatment of metals is well known from industrial experience. The results of metal leaching shown here suggest that an OPC/FA treatment provides suitable treatment for specific metals and that its preformance is unaffected by the presence of clay additives.

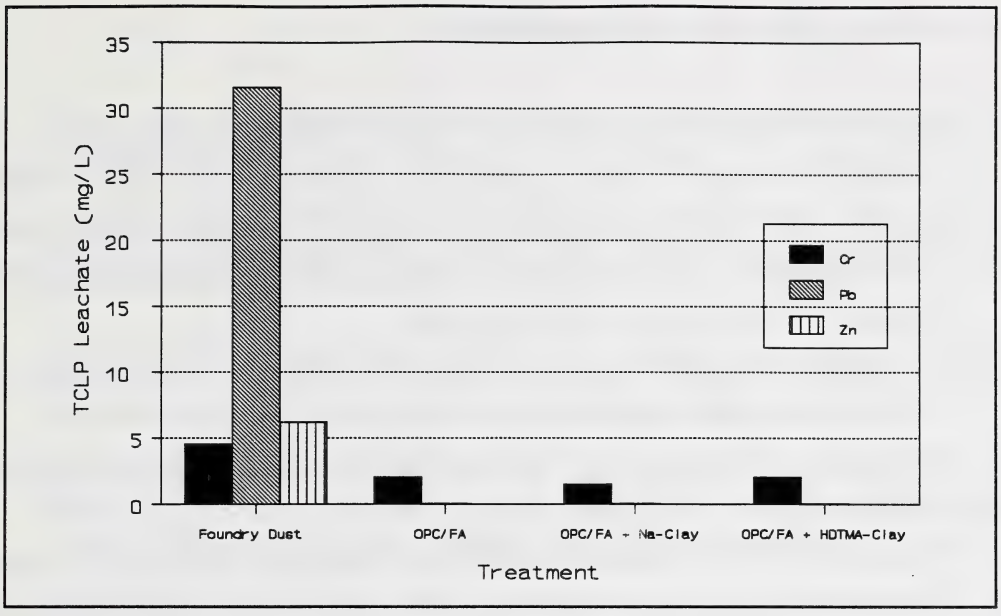


Figure 16. TLCP Leachate Metal Concentrations

CONCLUSIONS AND RECOMMENDATIONS

1) Unconfined compressive strength for the surrogate waste tested was a function of OPC content. Increasing OPC content caused a linear increase in unconfined compressive strength. TMA-Bentonite content accounted for a small portion of treatment variation.

2) HDTMA-Bentonite and CP-Bentonite showed a strong affinity for PCP and TCP compared to TMA-Bentonite and Na-Bentonite.

3) The Langmuir and Freundlich models of adsorption both provide an adequate description of the isotherms generated at the treatment levels tested.

4) Differences in behaviour of the various treated clays could be explained in terms of treatment chemical structure and properties.

5) Testing of the HDTMA-Bentonite/Cementitious treatment by a modified TCLP indicates that this treatment generates a leachate which is lower than regulatory criteria for hazardous waste by several orders of magnitude.

   A relatively small amount of HDTMA-Bentonite, 1.5 wt % of the treated waste, successfully treated a relatively high level of PCP contamination (700 mg/kg treated waste).

6) Metal containment by cementitious treatment was not affected by HDTMA-Bentonite for the metals and waste type studied.

   The study undertaken here indicates that organophilic clays show great promise for phenolic waste stabilization and that areas for future research include:

   a) examine HDTMA-Bentonite and CP-Bentonite for their potential to adsorb other classes of compounds;

   b) examine various quaternary ammonium compounds for their ability to modify bentonite at low cost;

   c) study the nature of adsorbate-adsorbent bonding and determine if adsorption is (relatively) irreversible;

   d) examine the long term *in situ* stability of treated wastes for biodegradation.

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